

Research of Adhesion Bonds Between Gas-Thermal Coating and Pre-Modified Base

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Abstract. Nature of adhesive bonds between gas-thermal nickel alloy coating and carbon steel base was examined using laser profilometry, optical metallography, transmission and scanning electron microscopy. The steel surface was plastically pre-deformed by an ultrasonic tool. Proved that ultrasound pre-treatment modifies the steel surface. Increase of dislocation density and formation of sub micro-structure are base elements of surface modification. While using high-speed gas-flame, plasma and detonation modes of coatings, surface activation occurs and durable adhesion is formed. Ultrasonic pre-treatment of base material is effective when sprayed particles and base material interact through physical-chemical bond formation. Before applying high-speed gas flame and plasma sprayed coatings, authors recommend ultrasonic pre-treatment, which creates periodic wavy topography with a stroke of 250 microns on the steel surface. Before applying detonation sprayed coatings, authors recommend ultrasound pre-treatment that create modified surface with a uniform micro-topography.

1. Introduction

In modern production, high-energy and high-speed gas-thermal spraying is widely used; before spraying surface preparation is performed by surface plastic deformation, designed for industrial production of machine parts. These methods are used for parts shape and surface finishing and compete with grinding and polishing [1]. Rolling and burnishing, diamond burnishing, regular surface microrelief formation, ultrasonic surface treatment - these methods simplify production of coated parts, since they do not require additional technological developments.

Before coating base layer surface pre-deformation is to be done with several objectives:

1. for gradient increase of base layer surface hardness so as to level material properties on the border between hard surface and soft base;
2. for base surface topography providing effective contact between a coating and a base material;



3. for mechanical activation of the surface by hardening and increasing the number of surface defects that increase adhesion bond areas and flow of physical and chemical processes as well as contribute to the bulk diffusion of materials;

4. for creation of compressive stress in subsurface layer and improving of fatigue resistance of coated parts [1-3].

Efficiency of surface treatment diminishes if temperatures, sufficient to remove effects of modifications, affect substrate while coating. However, in this case some beneficial effects may arise, for example, material structure improving, dislocation clusters redistribution and surface roughness optimization.

In the work a method of surface preparation for thermal coating is considered, namely, ultrasonic surface treatment with the indenter. The object of research is steel surface layer's structure after ultrasound treatment as well as interaction between coating and base material modified by surface deformation. Several methods of thermal coating were examined.

2. Materials and methods

Ultrasonic device UZGK-02 was used for preparation of surface basis for spraying. The ultrasonic device has a capacity of 200 W, indenter's vibration frequency 24 kHz, indenter's pressing force $F_N = 75$ N and vibration amplitude $\xi = 7$ microns. For surface treatment, a cylindrical steel sample was fixed in the lathe chuck and treated with ultrasonic instrument mounted in the lathe saddle. [4] Ultrasonic tool deformed and modified the surface layer as well as formed periodic topography. Microrelief controlled variables were set by rotary motion of the part at a rotation speed of 60 to 200 rev/min and ultrasonic instrument longitudinal feed at a rate of 0.05 mm/0.25 mm/rev. Samples were made from 20-carbon steel (0.2% of carbon) and 45-steel (0.45% of carbon).

Coating was performed by three methods: high-speed gas-flame, plasma and detonation [4-10]. Spraying modes were selected so as to achieve the most complete melting of the powder used and to provide the best coating quality. High-speed flame spraying was performed at the facility with the following characteristics: power 5 kW, fuel gas - propane; transporting gas - nitrogen, gas jet velocity at the nozzle exit - 800 m/s. Spraying was performed at a distance of 200mm; a linear velocity of torch movement 21 mm/s. The coating was formed by layers of 500-800mm [9].

Plasma spraying was performed with UPU-3D plasma torch with following specifications: power 30 kW; conveying plasma-forming gas - a mixture of argon and nitrogen; spraying distance of 100-150mm. Coating was performed in layers. Thickness of the sprayed coating was 1.000 micron [10].

A facility, developed at Institute of Hydrodynamics of SB RAS, was used for detonation spraying. The facility accelerates powder particles up to 1000 m/s. The coating was applied at a fixed (relative to the detonation gun jet) sample in the "spot" of 250 microns thickness. Sprayed surface was located at a distance of 100 mm from the nozzle [4]. A fuel mixture of acetylene and oxygen was used

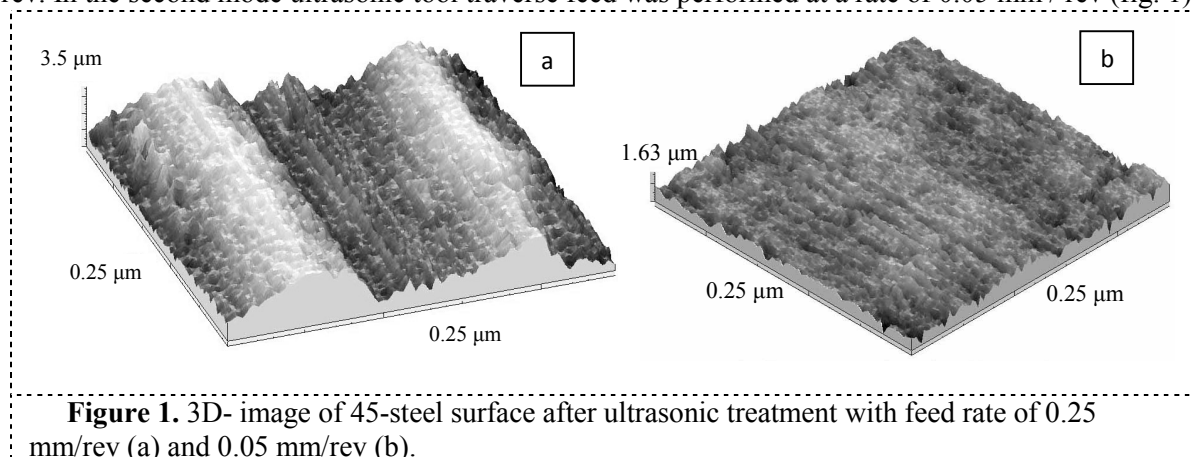
For spraying powders of pure metals were used, such as nickel, chromium, molybdenum, and nickel-based alloy PR-N70X17CP4 (Fe – 5 mass.%; C – 1.5 mass.%; Cr – 26 mass.%; Si – 2.3 mass.%; B – mass.3%; Ni – remaining) with a particle size of 30-50 micron. Examinations of base's morphology and roughness and analysis of its features after the coatings' interfacial failure were performed with a profilometry device «MICRO MEASURE 3D station». With a graphical program calculation of cold-welded regions' area was performed, in accordance with a predicted adhesive strength. Base surface condition after failure of coatings was examined using focused-beam microscope SEM «Philips SEM 515». The micro-hardness of the coating and the base was measured with «Nano Hardness Tester». With optical metallographic microscope Olympus GX-71 images of the coating and the base micro-cross section were obtained. Fine structure was examined with electron microscope Tesla BS-540 by transmission microscopy.

3. Results and discussion

Ultrasound treatment performs plastic deformation of steel surface. Periodic topography, conditioned by deformation grooves' superposition, is formed along longitudinal feed of the ultrasonic tool.

Periodic topography, conditioned by consistent indenter strokes, is formed along rotational movement of the part.

By changing ultrasound tool feed rate and workpiece rotation speed, you can change periodic topography parameters in two directions: longitudinal feed of the ultrasonic tool and workpiece rotational movement. In our research two processing modes were selected, both with rotation speed of 150 rev/min. In the first mode, ultrasonic tool longitudinal feed was performed at a rate of 0.25 mm / rev. In the second mode ultrasonic tool traverse feed was performed at a rate of 0.05 mm / rev (fig. 1).



In the first mode, after ultrasound treatment a topography is formed, which is a helical groove with micro-roughness interval of 0.25 mm. Roughness R_z 3.2 microns in direction of ultrasonic tool longitudinal feed; roughness R_z 0.7 microns in direction of rotational motion of parts (fig. 1a).

Topography with preset parameters provides high adhesion if coatings are formed from the highly heated liquids and particles sprayed at rates of 500 to 800 m/s while plasma and high-speed flame spraying. Flowing particles of sprayed material easily fill surface irregularities, crystallize or harden.

In the second mode, after ultrasonic treatment a uniform periodic topography is formed on the entire metal surface, without pronounced anisotropy, with roughness R_z 1.4 microns (fig. 1 b).

Topography with preset parameters provides high adhesion if coatings are formed from high- and low-heated particles deposited at rates of more than 800 m/s while detonation and gas-dynamic spraying. In this case, solid particles of sprayed material undergo plastic deformation on the base surface.

Adhesion of coatings, sprayed with high speed, is also determined by a surface activation level. While ultrasonic surface pre-treatment base surface structure modification occurs, resulting in surface activation. The process of sprayed particles adhesion to detail surface occurs as a first-order topochemical reaction. It occurs at interacting bodies' phase boundaries and is accompanied by substance's crystal lattice rearrangement [1, 11, 15]. The reaction rate and the completeness of its course depend on occurrence of defects in the reacting solid. These defects include dislocations, vacancies, grain boundaries, the surface itself and its sub micro-topography. Combinations of these defects, for example, surface dislocations, are the most favorable areas for topochemical reactions.

Let us see how ultrasonic treatment changes steel surface layer structure. Carbon steel structure is represented as a mixture structurally free ferrite and pearlite grains. Surface plastic deformation in the ultrasonic field causes grains' deformation reversal and shape changing in the surface layer to 30 microns. The upper parts of grains are extended by the forces of deformation displacement and adhesion between the workpiece and the tool, (fig. 2).

Nearer to the surface grains' deformation increases. On the surface grains become lamellae with length being ten times larger than thickness. By chemical etching, we identify light-colored ferrite and dark-colored pearlite lamellae, but formed sub-boundaries diminish image contrast, and quite often, the ferrite grains become dark (fig. 2). TEM shows what structural transformations occur with pearlite grains in the surface layer of steel (fig. 3). Initially pearlite structure is mainly lamellar consisting of

alternating cementite and ferrite laminae (fig. 3 a-d). Chaotically distributed dislocations with a density of $3 \cdot 10^9 \text{ cm}^{-2}$ are observed in ferrite laminae.

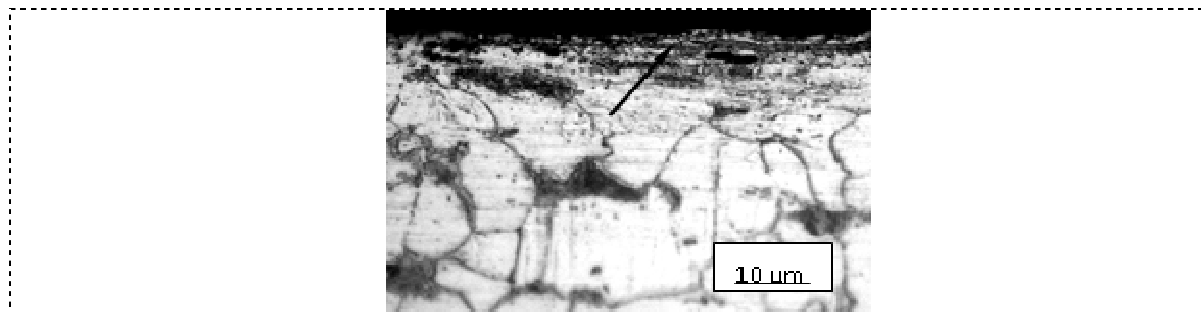


Figure 2. Metallographic image of 20-steel surface cross-section, after ultraviolet irradiation (region of plastic deformation is indicated by the arrow)

After ultrasonic treatment the following structural transformations (fig. 3 e-h) occur in the grains of pearlite. Fragmented substructure with fragments' size about 0.3 microns is formed in ferrite laminae. Cellular-mesh dislocation substructure with a scalar density $4 \cdot 10^{10} \text{ cm}^{-2}$ (fig. 3 e) is observed inside the fragments

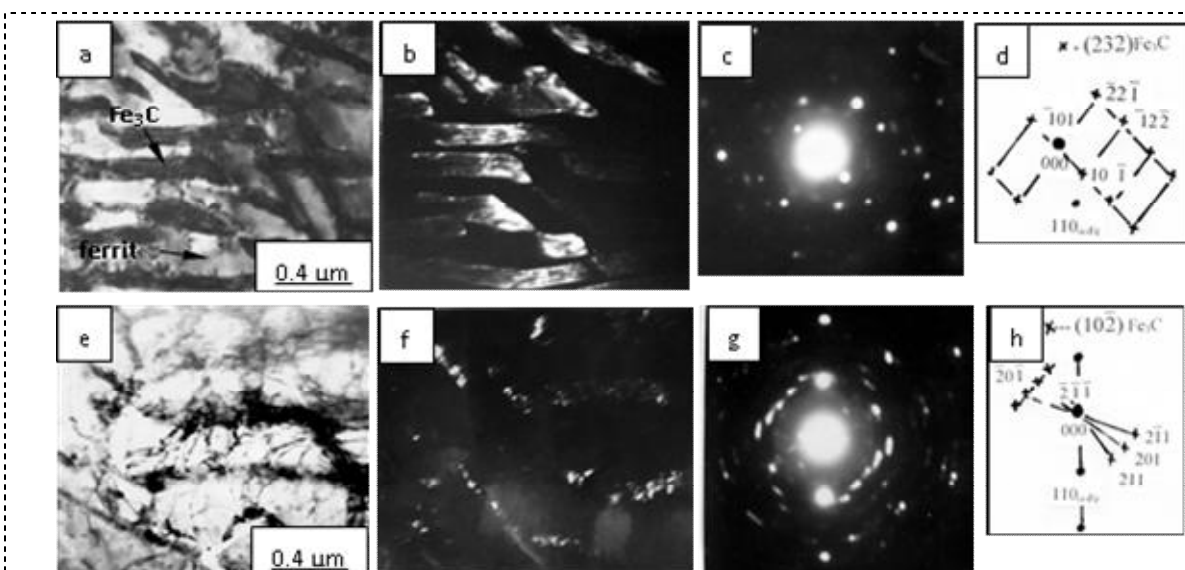


Figure 3. Electron microscopic image of pearlite grains in initial state (a-d) and on 20-steel surface after ultraviolet irradiation (e-h): a, e - bright-field image; b, f - dark-field image in one of Fe_3C reflexes; c, g - micro-diffraction picture; d, h - diagram of micro-diffraction picture

Cementite laminae are broken into individual nanoscale disordered particles (fig.3 f). Electron-diffraction examination of these particles shoes reflexes, which azimuthal deviation is about 10 degrees (fig. 3 g, h). Electron microscopy data confirm that plastic deformation with ultrasound vibrations modifies surface layer structure, namely, increases dislocations' density and forms sub microstructure. Described structural transformations provide activation of the steel surface [12].

Surface layer structure modification can be expressed in a gradient increase of micro-hardness values. On the surface micro-hardness can increase up by 100%. The hardened layer depth is as much as 100 microns.

Let us study how surface layer's structure and properties change after thermal sprayed coating. If any methods of coating, in the surface layer its structural features are sustained. As shown in fig. 4a, less contrast deformed area is sustained on the steel surface.

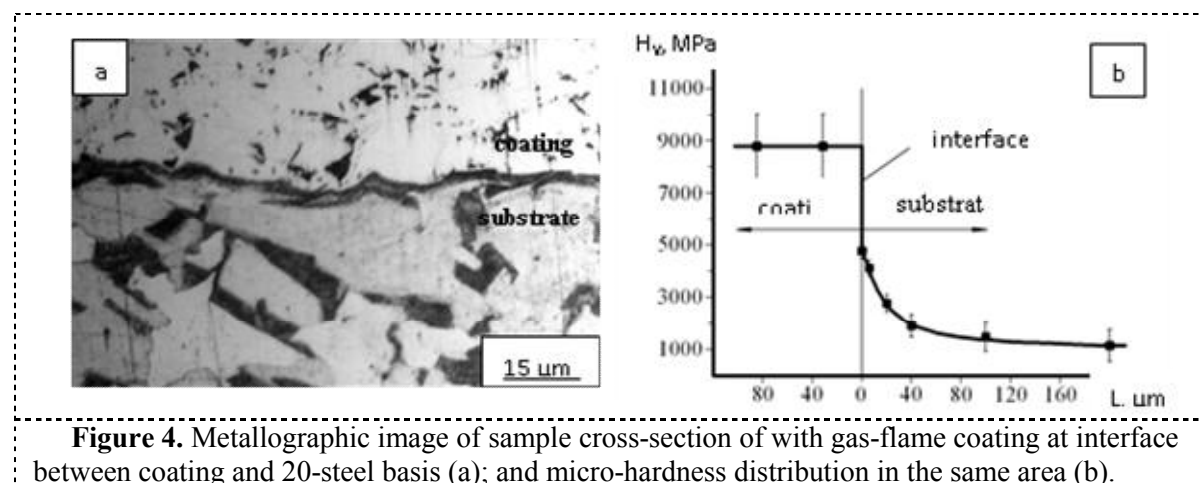


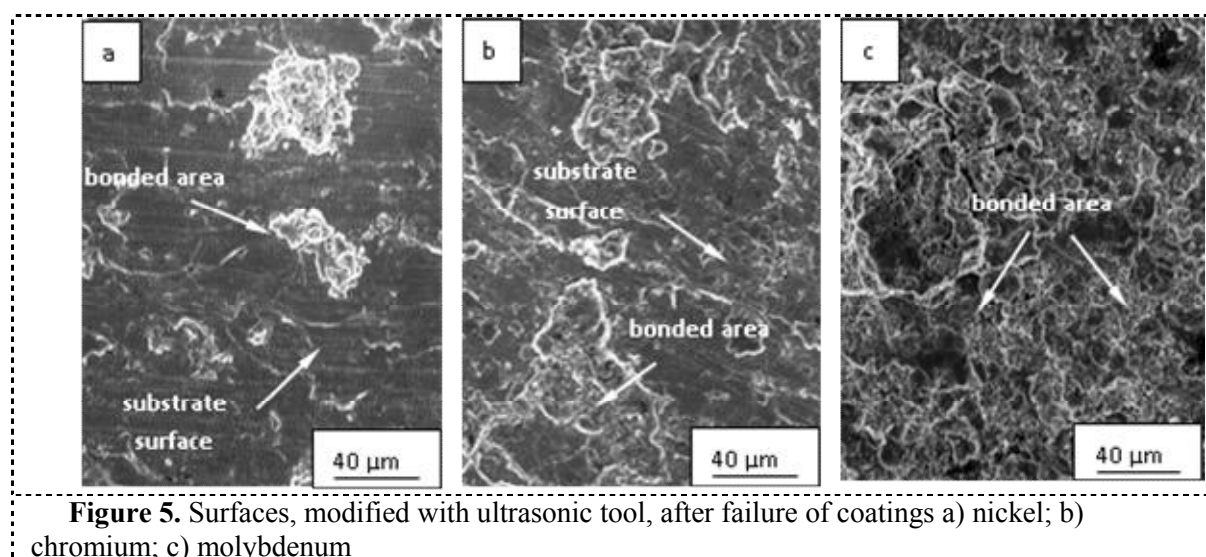
Figure 4. Metallographic image of sample cross-section of with gas-flame coating at interface between coating and 20-steel basis (a); and micro-hardness distribution in the same area (b).

Possibly, under applied shock and heating, additional deformation with returning and polygonization occurs in the steel surface layer. Available dislocation structure may transform into a perfect substructure with greater disorientation of sub grains and lower dislocation density. In any case, small size of structural objects, commensurate with sub microcrystalline size, is sustained. This creates a lower contrast while etching of surface layer (Figure 4 a). Also gradient increase of micro-hardness values is sustained in the steel surface layer (fig. 4b). As a result, after the gas-thermal sprayed coating, levelling of material properties on the boundary between hard surface and soft base occurs; that improves performance properties of the finished part. Sprayed coating adhesion was quantified by three-dimensional profilometry, which identified the total area of sprayed particles remaining in adhesion bonded areas after coating failure. Regions of adhesion between the surface and sprayed particles are characterized by cohesive coating failure and are interspersed with areas of adhesive coating failure. Proportion of these areas determines strength of adhesion of coating to base material.

In the first series of experiments, adhesion of nickel alloy coating, alloyed with chromium, silicon and boron, was tested. Before coating by gas-flame and plasma methods, ultrasonic pre-treatment was performed; this formed a periodic wavy topography, with strokes of 250 micron on the steel surface. Before coating by detonation method, pre-treatment was performed; that formed a modified surface with a uniform topography. The total area of adhesions between the coating and the base material was 38% after high-speed gas-flame spraying; and 40% after plasma spraying. This is comparable to adhesive strength of 40 MPa; it is considered to be a high-performance adhesion [9, 10]. After failure of the coating made by detonation method, the total area of seizures between coating and base material was 47%, which is comparable with adhesion strength of 47 MPa.

Greater adhesion between the detonation coating and the base is caused by specificity of particle deposition. High rate deposition of particles 1000 m/s provides additional surface activation due to shock plastic deformation [4].

A second series of tests was conducted to ascertain how particles' temperature affects interaction between the coating and the modified base; or how base heating with sprayed particles improves adhesion. For this task detonation coatings of refractory metals - nickel, chromium and molybdenum - were deposited on modified surfaces. Fig. 5 shows samples' surfaces after failure of the coatings; the image is obtained by scanning electron microscopy.



There are a various number of bonded areas on the base surface after coating failure. After the nickel coating failure, some fragments, commensurate with sprayed particles (fig. 5a), are sustained on the base surface. In the chromium coating, particles are fixed with agglomerates (fig. 5 b), which are difficult to be differentiated from adherent particles. This is caused by higher activity of the areas adjacent to pre-fixed particles. In this case, a single fixed particle is a nucleus of the agglomerate [12-16]. After molybdenum coating failure, the whole base surface is covered with remaining particles (fig. 5 c), so while contact between sprayed particles and base, nuclei make progress in growing into agglomerates.

It has been found that, after molybdenum powder coating failure, the total area of adhesion bond was about 80%; after chromium powder coating failure - about 40%; after nickel powder coating failure - less than 20%. Such a difference is caused by different melting points of the metals. Molybdenum particles ($t_{\text{m}} = 2620^{\circ}\text{C}$) heat the base material to penetration, thus ensuring the creation of metallic bond. Chromium ($t_{\text{m}} = 1860^{\circ}\text{C}$) and nickel ($t_{\text{m}} = 1455^{\circ}\text{C}$) particles are not welded to the base material; they form a strong physical-chemical bond. With such a mechanism of interaction, additional surface activation is necessary. Hence, ultrasonic pre-treatment is a substantial stage of the coating process.

4. Conclusions

Ultrasonic surface modification contributes to formation of reliable adhesive bonds while high-speed gas flame, plasma and detonation coatings. Surface modification manifests itself as increase of dislocation density and formation of submicrostructure.

For high-speed flame and plasma coating ultrasonic pre-treatment is recommended, forming periodic waved topography with interval of 0.25 mm. For detonation coating ultrasonic pre-treatment is recommend, forming uniform periodic topography. Ultrasound pre-treatment is effective if sprayed particles and the base form physical-chemical bonding.

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